

NO DRAWINGS

- (21) Application No. 36553/68 (22) Filed 31 July 1968
(31) Convention Application No. P 16 19 938.5 (32) Filed 1 Aug. 1967 in
(33) Germany (DT)
(45) Complete Specification published 21 April 1971
(51) International Classification C 08 g 47/02
(52) Index at Acceptance
C3T 6D11 6D1A 6F2 6H1 6H3 6H4B



(54) POLYORGANOSILOXANE COMPOSITIONS USEFUL
AS ANTI-FOAMING AGENTS

- 71 We, WACKER-CHEMIE G.m.b.H.,
a Company recognized by German Law, of
Postfach, Prinzregentenstrasse 22, 8 Munchen
22, Germany, do hereby declare the inven-
5 tion for which we pray that a patent may be
granted to us, and the method by which it is
to be performed, to be particularly described
in and by the following statement:—
It is known that mixtures of organopoly-
10 siloxanes and finely divided inorganic fillers
which have optionally been manufactured
with heating, can prevent, reduce or over-
come undesired foam formation.
This invention provides anti-foaming
15 agents based on organopolysiloxanes and
finely divided inorganic fillers which have the
advantages compared with the previously
known anti-foaming agents based on organo-
polysiloxanes and finely divided inorganic
20 fillers of being more effective, of retaining
their effectiveness for a longer period in the
presence of substances which have an
alkaline reaction and of being more easily
dispersible in water. They can therefore be
25 employed with more versatility and more
successfully than most previously known
anti-foaming agents.
The anti-foaming agents of the invention
comprise a mixture of an organopolysiloxane
30 and a finely divided inorganic filler and in
addition contain 0.5 to 12% by weight, based
on the weight of the organopolysiloxane, of
a magnesium, aluminium, calcium, zinc or
scandium salt of an aliphatic monobasic car-
35 boxylic acid or hydroxy carboxylic acid
having 12 to 22 carbon atoms.
As organopolysiloxane, it is possible to use,
for the manufacture of the anti-foaming
agents according to the invention, any of the
40 liquid organopolysiloxanes which have hith-
erto been used for the preparation of anti-
foaming agents based on organopolysilox-
anes. In the preferred organopolysiloxanes
80 to 99 mol per cent of the siloxane units
45 are diorganosiloxane units and 1 to 20 mol
per cent of the siloxane units, that is to say
the remaining siloxane units are triorgano-
siloxane units. Up to 10 mol per cent of the
diorganosiloxane units may, however, be re-
placed by other polymer units such as mono- 50
organosiloxanes and/or $\text{SiO}_{1/2}$ units. The tri-
organosiloxane units may be partially or
completely replaced by units of general
formula $\text{R}_2\text{Si}(\text{OR}')\text{O}_{1/2}$, wherein each R is
an SiC-bonded organic radical and R' is an 55
alkyl radical having 1 to 5 carbon atoms,
an aryl radical, especially a phenyl radical,
or a hydrogen atom.
Because of their easy accessibility methyl
radicals are preferred as SiC-bonded organic 60
radicals in the organopolysiloxanes; these
methyl radicals may however be partially
or completely replaced by other organic
radicals, especially hydrocarbon radicals, for
example, ethyl and/or 2-phenylpropyl radi- 65
cals. Vinyl radicals may also be present in
the triorganosiloxy groups for example, as in
the vinyltrimethylsiloxy group.
The viscosity of the organopolysiloxanes is
preferably 35 to 100,000 cSt/25°C. 70
As finely divided inorganic fillers it is pos-
sible to use any of the finely divided in-
organic fillers, that is to say fillers having a
particle size of at most 25 microns, that have
hitherto been used for the preparation of 75
anti-foaming agents based on organopoly-
siloxanes and finely divided inorganic fillers
or have been recommended for this purpose.
Especially good results are achieved with
finely divided oxides of silicon, aluminium or 80
zinc. Silicon dioxide, especially silicon di-
oxide manufactured pyrogenically in the gas
phase, silicic acid hydrogel dehydrated whilst
retaining the structure, that is to say so-
called "silicon dioxide aerogel", or pre- 85
cipitated silicon dioxide, is preferred because
of its easy accessibility and because very good
results are achieved with it. Instead of or in
addition to the inorganic fillers hitherto men-
tioned it is possible to use other solid inert 90

finely divided inorganic substances, for example, magnesium silicate, magnesium aluminium silicate or carbon black. The finely divided inorganic fillers are used in amounts of 0.1 to 30% by weight, especially 0.3 to 5% by weight, based on the weight of the organopolysiloxanes.

The anions in the salts used in accordance with the invention may be represented by the general formula $R''COO-$, wherein R'' is an aliphatic hydrocarbon residue having 11 to 21 carbon atoms which is optionally substituted by a hydroxyl group. The following may be mentioned as examples of aliphatic carboxylic acids or hydroxy carboxylic acids having 12 to 22 carbon atoms, that is to say of fatty acids or hydroxy-fatty acids from which the salts used according to the invention can be manufactured: lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, hydroxystearic acid, the commercially available mixtures of aliphatic saturated monocarboxylic acids which are branched in the α -position to the carboxyl group and have 15 to 19 carbon atoms per molecule, the commercially available carboxylic acids obtained by oxidation of products manufactured by the oxo synthesis, which are branched in other positions than in the α -position to the carboxyl group and have 12 to 15 carbon atoms, and also linoleic acid, linolenic acid, oleic acid and ricinoleic acid. Stearic acid and 12-hydroxystearic acid are preferred because of their easy accessibility.

The salts may be neutral salts, for example, aluminium tripalmitate or basic salts, for example, aluminium monopalmitate and aluminium dipalmitate. It is possible to use mixtures of different salts. The best results are achieved if the melting point of the salt does not exceed 180°C.

The salt is preferably employed in amounts of 1.5 to 5% by weight relative to the weight of the organopolysiloxanes. The weight ratio of salt to the finely divided inorganic fillers is preferably 0.3 : 1 to 5.0 : 1, corresponding to 30 to 500% by weight based on the weight of the fillers.

Many salts of the type to be used in accordance with the invention are commercially available.

The anti-foaming agents according to the invention may optionally additionally contain any desired conventional organic anti-foaming agents, for example, tributyl phosphate.

The best results are achieved if during mixing or after mixing the constituents the mixture of the constituents of the anti-foaming agents according to the invention is warmed to a temperature at or above the melting point of the particular fatty acid or hydroxy-fatty acid salt used. During this warming however a temperature of 250°C should not be exceeded. In general the material will be

heated to at least 150°C. Heating preferably lasts 10 minutes to 10 hours, generally 2 to 5 hours. The sequence of addition of the constituents during the manufacture of the anti-foaming agents according to the invention is not a decisive factor.

If the material is not heated during the mixing it is advantageous if after the heating the constituents are again mixed as thoroughly as possible with one another in mixing equipment, for example, of the type that is usually employed for the manufacture of anti-foaming agents based on organopolysiloxanes and finely divided inorganic fillers, for example, a mixing vessel equipped with a simple stirrer, or a planetary stirrer unit.

The anti-foaming agents according to the invention may be used to prevent, reduce or combat foam, especially in aqueous solutions, in the undiluted form, in the form of dispersions in organic solvents, for example, aliphatic hydrocarbons boiling in the range of 50°C to 250°C at 760 mm Hg (absolute), aromatic hydrocarbons, for example benzene, toluene, xylene or trimethylxylenes, and ethers which are suitable for use as solvents such as di-*n*-butyl ether and ethylene glycol dimethyl ether, in the form of aqueous dispersions of the oil in water type produced with the acid of dispersing agents, for example, protective colloids, for example, polyvinyl alcohol which optionally still contains up to 40 mol per cent of acetyl groups, or methyl cellulose and/or emulsifiers, for example, stearyl polyoxyethylene glycol ether, cetyl polyoxyethylene glycol ether, sorbitane monostearate, trimethylnonyl polyoxyethylene glycol ether or nonylphenol polyoxyethylene glycol ether, in the form of free-flowing powders manufactured by drying such dispersions or in the form of free-flowing powders which have been manufactured by mixing protective colloids in the dry state with the anti-foaming agents according to the invention.

The anti-foaming agents according to the invention may be employed for the prevention or reduction or removal of foam, for example, in the evaporation of alkaline waste lyes in the paper industry, in the concentration of rubber latices, in cutting oil emulsions in the metal-working industries, in dispersion dyestuffs and other end uses of synthetic resin dispersions, in the refining of sugar, in conveying petroleum, in textile ryeing, in the disposal of waste water, in food manufacture, in fermentation processes such as the manufacture of antibiotics, in the floatation of ores and in the digestive tract of human beings and animals.

The following Examples illustrate the invention:

Example 1

3 kg of a dimethylpolysiloxane with the

ends blocked by trimethylsiloxy groups, having a viscosity of 9,000 cSt/25°C, are mixed with 70g of aluminium dipalmitate and 60g of aluminium oxide having a particle size of 0.005 to 0.03 microns on a triple-roll mill. The mixture thus obtained is then heated for 2 hours at 185°C in a drying cabinet and is thereafter stirred in a planetary stirrer unit until a uniform paste forms.

0.5 g of this mixture are dispersed in 10 cm³ of ethyl acetate and added to a strongly foaming solution of 5 g of a nonylphenol polyethylene glycol ether commercially available as an emulsifier and having 4 to 30 oxyethylene units per molecule, in 5 l of water. After a brief thorough shaking the foam has been completely removed.

Example 2

(a) 2 kg of a dimethylpolysiloxane having an ethoxy group in each terminal unit and a viscosity of 550 cSt/25°C, are mixed for 10 minutes in a planetary stirrer unit with 80 g of zinc behenate and 50 g of silicone dioxide having a surface area (BET/compare Brunauer, Emmet and Teller, Journ. Am. Chem. Soc., Volume 60, Page 309) of 130 g/m² and an average particle size of about 0.03 microns. The mixture thus obtained is then heated for 1 hour at 150°C in a drying cabinet and is subsequently stirred in a planetary stirrer until a uniform paste is formed (Paste A).

(b) For comparison, the procedure described above is repeated with the modification that no silicon dioxide is conjointly used (Paste B).

(c) Again for comparison, the procedure described above under (a) is repeated with the modification that no fatty acid salt is conjointly used (Paste C).

0.5 g of each of these pastes are dispersed in 10 cm³ of toluene at a time and added to 5 l at a time of the emulsifier solution described in Example 1. After shaking ten times with a dispersion of Paste A, the foam collapses completely within a few seconds, with a dispersion of Paste B a 4 cm high foam persists and with a dispersion of Paste C a 2 cm high foam persists.

Example 3

4 kg of a dimethylpolysiloxane having an Si-bonded hydroxyl group in each terminal unit and a viscosity of 3500 cSt/25°C, are first mixed with 130 g of calcium 12-hydroxystearate and then with 85 g of silicone dioxide of the type described in Example 2, in a planetary stirrer unit. The mixture thus obtained is then heated for 30 minutes at 180°C in a drying cabinet and is subsequently stirred in a planetary stirrer unit until a viscous uniform mass has been produced.

400 g of this mass together with 100 g of a cetyl polyoxyethylene glycol ether having an average of about 10 oxyethylene units are dispersed in 1500 cm³ of water by means

of a high-speed mixing apparatus to give an anti-foaming agent in the form of an aqueous emulsion.

WHAT WE CLAIM IS:

1. An anti-foaming agent comprising an organopolysiloxane, 0.1 to 30% by weight, based on the organopolysiloxane, of a finely divided (as hereinbefore defined) inorganic filler and 0.5 to 12% by weight, based on the weight of the organopolysiloxane, of a magnesium, calcium, aluminium, zinc or scandium salt of an aliphatic monobasic carboxylic acid or hydroxy carboxylic acid having 12 to 22 carbon atoms.

2. An anti-foaming agent as claimed in claim 1, wherein the organopolysiloxane consists of 80 to 99 mol per cent of diorganosiloxane units and 1 to 20 mol per cent of triorganosiloxane units.

3. An anti-foaming agent as claimed in claim 2, wherein up to 10 mol per cent of the diorganosiloxane units are replaced by monoorganosiloxane units and/or SiO₂ units.

4. An anti-foaming agent as claimed in claim 2 or claim 3, wherein some or all of the triorganosiloxane units are replaced by units of the general formula R₂Si (OR')O_{1/2}, wherein each R is an SiC-bonded organic radical and R' is an alkyl radical containing 1 to 5 carbon atoms, an aryl radical or a hydrogen atom.

5. An anti-foaming agent as claimed in any one of claims 1 to 4, wherein the organic radicals in the organopolysiloxane are methyl radicals.

6. An anti-foaming agent as claimed in any one of claims 1 to 5, wherein the viscosity of the organopolysiloxane is within the range of from 35 to 100,000 cSt/25°C.

7. An anti-foaming agent as claimed in any one of claims 1 to 6, wherein the filler is a finely divided oxide of silicon, aluminium or zinc or is magnesium silicate magnesium aluminium silicate or carbon black.

8. An anti-foaming agent as claimed in claim 7, wherein the filler is silicon dioxide.

9. An anti-foaming agent as claimed in claim 8, wherein the filler is silicon dioxide that has been manufactured pyrogenically in the gas phase, silicic acid hydrogel that has been dehydrated whilst retaining its structure or precipitated silicon dioxide.

10. An anti-foaming agent as claimed in any one of claims 1 to 9, wherein the filler is present in an amount within the range of from 0.3 to 5% by weight based on the weight of the organopolysiloxane.

11. An anti-foaming agent as claimed in any one of claims 1 to 10, wherein the metal salt is a salt of stearic acid or 12-hydroxystearic acid.

12. An anti-foaming agent as claimed in any one of claims 1 to 11, wherein the melting point of the salt does not exceed 180°C.

13. An anti-foaming agent as claimed in any one of claims 1 to 12, wherein the metal salt is present in an amount within the range of from 1.5 to 5% by weight based on the weight of the organopolysiloxane.

14. An anti-foaming agent as claimed in any one of claims 1 to 12, wherein the weight ratio of metal salt to filler is within the range of from 0.3 : 1 to 5 : 1.

15. An anti-foaming agent as claimed in claim 1, substantially as described in any one of the Examples herein.

16. A process for the manufacture of an anti-foaming agent as claimed in claim 1, which comprises mixing together an organopolysiloxane, 0.1-30% by weight based on the organopolysiloxane a finely divided inorganic filler and 0.5 to 12% by weight based on the weight of the organopolysiloxane of a magnesium, calcium, aluminium, zinc, or scandium salt of an aliphatic monobasic carboxylic acid or hydroxycarboxylic acid having 12 to 22 carbon atoms and during or after the mixing heating the material to a temperature above the melting point of the metal salt used but below 250°C.

17. A process as claimed in claim 16, wherein the heating operation is carried out after the material has been mixed and the material is remixed after the heating operation.

18. A process as claimed in claim 16 or claim 17, wherein the mixture is heated to a temperature of at least 150°C.

19. A process as claimed in any one of claims 16 to 18, wherein the material is heated for a period within the range of from 10 minutes to 10 hours.

20. A process as claimed in claim 19, wherein the material is heated for a period within the range of from 2 to 5 hours.

21. A process as claimed in claim 16, conducted substantially as described in any one of the Examples herein.

22. A process for the prevention, reduction or removal of foam in a material that is liable to foam which comprises adding to the material an anti-foaming agent as claimed in any one of claims 1 to 15.

23. A process as claimed in claim 22, wherein the anti-foaming agent is added in its undiluted form, in the form of a dispersion in an organic solvent, in the form of an aqueous dispersion of the oil in water type produced with the aid of dispersing agents and/or emulsifiers, in the form of a free flowing powder which has been manufactured by drying such a dispersion or in the form of a free flowing powder which has been manufactured by mixing a protective colloid in the dry state with the undiluted anti-foaming agent.

ABEL & IMRAY
Chartered Patent Agents,
Northumberland House,
303-306 High Holborn,
London, W.C.1.